JAPANESE [JP,11-222402,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

EXAMPLE

[Example]This invention is not limited by these examples although this invention is explained more below at details based on an example.
Example 1 [preparation of bridge construction hydrophilic polymer particles] acrylamide 4g (0.056-mol and 72.2-mol %), The methylenebis acrylamide 2.4g (0.0156-mol and 20.1-mol %), And the mixed liquor of 1.6 g (0.006-mol and 7.7-mol %) of 4-(N,N-diethyl dithiocarbamate) styrene, It added to 86 ml of ethanol, and the mixed solvent of 6 ml of water, and the precipitate polymerization was carried out at the temperature of 60 ** among argon atmosphere for 17 hours using 0.05 g of azobisisobutyronitrile. In this reaction, after heating in temperature of 60 **, after about 2.5-hour progress, the polymerization system became cloudy and the polymer particle generated.
[0044][Hydrolysis] 100 ml of ethanol, 50 ml of water, and the mixed liquor of 2 g of sodium hydroxide were added, among argon atmosphere, after agitating into reaction mixed liquor for 5 hours and hydrolyzing into it at the temperature of 70 **, it centrifuged into it and 100 ml of ethanol and the mixed solvent of 100 ml of

water washed precipitate particles twice into it. In order to make a sulfhydryl group generate, precipitate particles were added in water, 1N-chloride was added, and pH was adjusted to about 5, and it agitated one whole day and night, and hydrolyzed. Subsequently, mixed liquor was centrifuged, 100 ml of ethanol and the mixed solvent of 100 ml of water washed precipitate particles 3 times, and 150 ml of water washed twice further.

[0045]Particles were colored thin orange, when the mixed liquor of the silver nitrate 1.05g (0.006 mol) and 150 ml of water was added to the precipitate particles which [silver complex support polymer particle prepared] washed and it agitated at the room temperature to them for 2 hours. By centrifuging mixed liquor, washing precipitate particles twice and carrying out reduced pressure drying with 150 ml of methanol, once, with 150 ml of water, The silver complex support polymer particle (mean particle diameter of about 60-90 nm) was obtained (the yield of 7.8 g (dry solid conversion), 14.9 % of the weight of moisture contents, 22.8 % of the weight of silver content, 89.9% of yield).

[0046]Example 2 [preparation of bridge construction hydrophilic polymer particles] acrylamide 4g (0.056 mol), The methylenebis acrylamide 2.4g (0.0156 mol) and the mixed liquor of 1.6 g (0.0152 mol) of 4-vinylpyridine, It added to 86 ml of ethanol, and the mixed solvent of 6 ml of water, and the precipitate polymerization was carried out at the temperature of 60 ** among argon atmosphere for 17 hours using 0.05 g of azobisisobutyronitrile. In this reaction, after heating in temperature of 60 **, after about 1.5-hour progress, the polymerization system became cloudy and the polymer particle generated. Reaction mixed liquor was centrifuged and 150 ml of water washed precipitate particles twice.

[0047]To the precipitate particles which [silver complex support polymer particle prepared] washed, the mixed liquor of the silver nitrate 2.58g (0.0152 mol) and 150 ml of water is added, and it agitates at a room temperature for 2 hours, and is **. The silver complex support polymer particle (mean particle diameter of about 90-120 nm) was obtained by centrifuging mixed liquor, washing precipitate particles twice and carrying out reduced pressure drying with 150 ml of methanol (the yield of 8.6 g (dry solid conversion), 13.3 % of the weight of moisture contents, 35.2 % of the weight of silver content).

[0048]Example 3 [preparation of bridge construction hydrophilic polymer particles] acrylamide 4.5g (0.063 mol), The mixed liquor of the methylenebis acrylamide 2.4g (0.0156 mol) and the acrylic acid 1.1g (0.0152 mol), It added to 86 ml of ethanol, and the mixed solvent of 6 ml of water, and the precipitate polymerization was carried out at the temperature of 60 ** among argon atmosphere for 17 hours using 0.05 g of azobisisobutyronitrile. In this reaction,

after heating in temperature of 60 **, after about 0.5-hour progress, the polymerization system became cloudy and the polymer particle generated. Reaction mixed liquor was centrifuged and 150 ml of water washed precipitate particles twice.

[0049]To the precipitate particles which [silver complex support polymer particle prepared] washed, the mixed liquor of the silver nitrate 2.58g (0.0152 mol) and 150 ml of water is added, and it agitates at a room temperature for 2 hours, and is **. The silver complex support polymer particle (mean particle diameter of about 90-120 nm) was obtained by centrifuging mixed liquor, washing precipitate particles twice and carrying out reduced pressure drying with 150 ml of methanol (the yield of 11.5 g (dry solid conversion), 13.9 % of the weight of moisture contents, 25.7 % of the weight of silver content).

[0050][Antibacterial evaluation] According to the Japanese Society of Chemotherapy standard method, the minimum growth alienation concentration (Media Interface Connector, ppm) estimated antibacterial properties as follows.

(1) The silver complex support polymer particle comparative example 1 acquired in sample examples 1-3 : a commercial silver silica gel system antimicrobial agent (about 3 % of the weight of the amounts of silver ions)

Comparative example 2: A commercial silver zeolite system antimicrobial agent (about 3 % of the weight of the amounts of silver ions)

(2) use strain Staphylococcus: -- Staphylococcus . Aureus (Staphylococcus aureus) 209P JC-1 Escherichia coli: ESHIRISHIA The bouillon culture medium for Cori (Escherichia coli) NIHJ JC-2

(3) culture-medium susceptibility measurement and the agar medium for sensitivity discs were used.

(4) Since test-method each sample was insolubility, it was suspended to purified water and the suspension of the 10 time concentration of examination concentration was prepared. When examining, it mixed and used at a rate of examination suspension 1 part by volume to culture-medium 9 part by volume. On the other hand, after cultivating one nights of test organisms at 37 ** using a susceptibility bouillon culture medium, it diluted with the culture medium suitably, and 10^6 cfu/ml test organism liquid was prepared. A result is shown in Table 1.

[0051]

[Table 1]

表 1

菌株	最小発育阻止濃度 (MIC, ppm)				
	実施例1	実施例2	実施例3	比較例1	比較例2
S. aureus	1000	250	2000	>8000	4000
E. coli	500	250	2000	>8000	4000

In the antimicrobial polymer particle of Examples 1-3, high antibacterial properties are revealed compared with a commercial item so that clearly from Table 1.

[0052]Silver complex support polymer particle 1 weight section obtained in example 4 Example 2 and ultraviolet curing type paint (Toagosei make, ARONIKKUSU UV-3701) 99 weight section are mixed, The obtained dispersion mixing liquid was applied to the polyethylene terephthalate film by the bar coating machine, and the hardening layer was formed by irradiating with ultraviolet rays for 10 minutes using a high-pressure mercury lamp.

It replaced with the silver complex support polymer particle of comparative example 3 Example 2, and the hardening layer was formed like the above except using the antimicrobial agent of the comparative example 2.

[0053]Silver complex support polymer particle 1 weight section obtained in example 5 Example 2 and aqueous emulsion coating material (Toagosei make, Aaron NS-1200) 99 weight section (solid content conversion) are mixed, The obtained dispersion mixing liquid was applied to the polyethylene terephthalate film by the bar coating machine, it dried at the room temperature, and the coating film was formed.

It replaced with the silver complex support polymer particle of comparative example 4 Example 2, and the coating film was formed like the above except using the antimicrobial agent of the comparative example 2.

[0054]And the antibacterial properties of the coat film to said strain were investigated as follows. Staphylococcus. (Staphylococcus .) After cultivating aureus (Staphylococcus aureus) 209P JC-1 and 37 ** of Escherichia coli (ESHIRISHIA Cori (Escherichia coli) NIHJ JC-2) by a nutrient broth culture medium (NB, Nutrition research) for 18 to 20 hours, It diluted with the nutrient broth culture medium (NB, Nutrition research) diluted to the concentration 1/500 suitably, and 10^5 cfu/ml test organism liquid was prepared. Put 1 ml of test organism liquid into an eye TSUKIN plastic petri dish (Sumilon) 35 mm in diameter, turn the film surface of the above-mentioned sample coat down, and test organism liquid was made to contact, after lower, the seal of the lid was carried out to the petri dish, and it was allowed to stand at the room temperature (25 **) on it for 24 hours. It was operated like the above, using (no

processing) only in fungus liquid as contrast. The number of microorganism at the time of a start and the number of microorganism after 24-hour progress were measured by ****** using a nutrient agar medium (NA, Nutrition research), and change of the number of microorganism estimated the germicidal action. The antibacterial properties of a coat are shown in Table 2.

[0055]

[Table 2]

表 2

	菌株の種類	接触時間	
		0 h	24 h
実施例4	S. aureus	4.3×10^5	< 10
比較例3		4.3×10^5	1.5×10^5
実施例5		4.3×10^5	<10
比較例4		4.3×10^5	3.8×10^5
対照(無処理)		4.3×10^5	7.7×10^5
実施例4	E. coli	1.7×10^5	<10
比較例3		1.7×10^5	1.1×10^6
実施例5		1.7×10^5	< 10
比較例4		1.7×10^5	3.5×10^5
対照(無処理)		1.7×10^5	1.5×10^7

In the antimicrobial polymer particle of an example, high antibacterial properties are revealed compared with a commercial item so that clearly from Table 2. The hardening layer formed in Example 4 was a high hardening layer of transparency except having colored it yellow a little. On the other hand, the hardening layer formed by the comparative example 3 was colored reddish brown, and transparency also fell. Thus, in the antimicrobial polymer particle of Example 2, probably because a silver ion exists as a complex, it is stable to ultraviolet rays. Particle diameter is dramatically small, since particles are moreover formed with the organic high polymer, the antimicrobial polymer particle of Example 2 does not have a difference of a refractive index with base resin (ultraviolet curing type resin), and its transparency is high. On the other hand, since the antimicrobial agent of the comparative example 2 has the small stability of a silver ion, coloring arises, and since it is as large as the particle diameter of about 1-3 micrometers and the difference of a refractive index with base resin is moreover also large, transparency is falling.

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